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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 4/29/91	3. REPORT TYPE AND DATES COVERED
4. TITLE AND SUBTITLE "The Impact of Interphase Mass-Transfer Rate and Equilibrium for Multiphase Groundwater Systems"			5. FUNDING NUMBERS DAAL03-88-K-0002
6. AUTHOR(S) Cass T. Miller			7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) The University of North Carolina-Chapel Hill Department of Environmental Sciences and Engineering CB #7400, Rosenau Hall Chapel Hill, N.C. 27599-7400
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211			8. PERFORMING ORGANIZATION REPORT NUMBER 62
11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.			10. SPONSORING/MONITORING AGENCY REPORT NUMBER AL0 24469.1-65
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE

1. ABSTRACT (Maximum 200 words)

Groundwater contamination by substances that are immiscible with water (e.g., gasoline, jet fuels, chlorinated solvents) is well-documented as a commonplace occurrence. The release of such nonaqueous phase liquids (NAPLs) leads to a multiphase system in which contaminants can exist in, move within, and be transport among a NAPL phase, an aqueous phase, a gas phase, and solid phase. A common assumption until now is that each chemical species is in local equilibrium among all the phases present in a subsurface environment.

This research project investigated the propriety of the local equilibrium assumption through conduct of fundamental laboratory studies and mathematical modeling of interphase mass transfer in multiphase porous media systems. The experimental results of this work were used to develop interphase mass transfer rate coefficient correlations for NAPL-aqueous and aqueous-vapor systems, and to determine correlations of NAPL morphology at residual saturation. The modeling portion of this study incorporated the experimental results into one- and two-dimensional multiphase flow and transport models—in order to investigate expected deviations from equilibrium conditions at the field scale. Experimental and modeling results showed that deviations from equilibrium are common for vapor-aqueous phase mass transfer and may be important for NAPL-aqueous phase mass transfer, especially in heterogeneous systems.

14. SUBJECT TERMS			15. NUMBER OF PAGES 8
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

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**The Impact of Interphase Mass-Transfer Rate and
Equilibrium for Multiphase Groundwater Systems**

Final Report

Cass T. Miller, Principal Investigator

29 April 1991

U.S. Army Research Office

Grant Number: DAAL03-88-K-0002

The University of North Carolina-Chapel Hill
Department of Environmental Sciences and Engineering

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Statement of Problem Studied

The groundwater resources of the United States have been extensively contaminated by a wide variety of organic pollutants. This widespread contamination has led to a need for a better understanding of the processes that impact the transport and eventual fate of such contaminants. A better understanding of these fundamental processes is necessary to accomplish more accurate assessment of health risks, and more economical and effective design of aquifer renovation measures.

One of the most common, and most challenging, groundwater contamination problems results from the spill of a substance that is immiscible with water. Immiscible contaminants (nonaqueous phase liquids or NAPLs) are frequently introduced into groundwater systems by leaking underground storage tanks, the associated appurtenances, or other direct releases. Once released, an immiscible solvent begins a complex path of transport and transformation. Accurate description of the resulting multiphase groundwater system is a requisite for describing the time dependent mass, and distribution of contaminant mass—an important objective. To this end, a need exists to better understand interphase mass transfer phenomena in such systems.

The treatment of multiphase systems has traditionally been within the realm of the oil industry, but the need to protect groundwater quality has changed this division. The motivation of the oil industry work has been to remove as much of the immiscible product from the subsurface as possible, and this work has usually neglected the interphase mass transfer of components of the immiscible organic phase to the aqueous phase. The study of multiphase groundwater systems is oriented differently—to determine the impact of a NAPL on the aqueous phase.

The motivation for this investigation was the typical treatment of solute transport in multiphase systems as linear equilibrium processes. Significant evidence existed to suggest that the assumption of a rapidly-attained, linear equilibrium between phases is a gross oversimplification for some situations. This study sought to quantitatively elucidate the effects of nonequilibrium mass transfer conditions in subsurface systems.

The goal of the project was met through conduct of fundamental laboratory investigations of multiphase mass transfer processes, which are operative in subsurface systems. This investigation focused on the collection and analysis of a detailed set of quantitative data on the final phase equilibrium and the rate of approach to that equilibrium for multiphase mass transfer reactions. NAPL-aqueous, NAPL-solid, and aqueous-vapor phase processes were given primary consideration.

Summary of Most Important Results

Overview

As noted in the publication section of this report, a large quantity of significant and publishable new information was developed during this research project. This section will briefly summarize the most important major findings of this work. Details of procedures used, data gathered, and full discussions of data analysis and interpretations can be found by reference to the project documents produced to date and other documents currently in preparation. This brief summary will be grouped into: NAPL-aqueous phase mass transfer, residual saturation morphology, and aqueous-vapor mass transfer.

NAPL-Aqueous Mass Transfer

As is well known now, once an immiscible fluid is released in the subsurface it tends to move vertically through the unsaturated zone, leaving a portion of the pore space filled with NAPL that is held immobile by capillary forces. Thus over a relatively short time period—compared to the total time the multiphase fluid persists in the subsurface—the multiphase fluid becomes trapped in a state of residual saturation. A major route of subsurface contamination occurs through dissolution of the trapped NAPL into the aqueous phase that flows through the NAPL-contaminated region.

A significant portion of this work dealt with the measurement and modeling of the NAPL-aqueous phase dissolution process. This is significant because of the large number of sites that are contaminated with fluids that are immiscible with water. A paper by Miller et al. (1990) details the experimental procedures used to measure the dissolution process, the development of dimensionless variables that characterize the process, and the derivation of an empirical relationship that allows for the estimation of mass transfer characteristics as a function of the relevant physical and chemical properties of a system.

Mayer and Miller published two papers on the development and application of a general multiphase flow and transport model. The NAPL-aqueous phase dissolution process was included in this model and the laboratory-derived constitutive relationship was used to estimate typical mass transfer coefficients.

The results of both the experimental and modeling work show that NAPL-aqueous phase mass transfer is relatively fast compared to the space and time scales of concern in typical subsurface systems. Using typical parameters for groundwater flow, a groundwater phase moving through a zone of uniformly trapped NAPL would be expected to reach equilibrium with the NAPL phase within a fraction of a meter. This suggests that for such conditions equilibrium between the water and the NAPL phase is a reasonable assumption.

An unanswered and potentially very important question coming from this work is the effect of subsurface heterogeneity on achievement of equilibrium. That is heterogeneity of both the NAPL distribution and the porous media system would be expected to cause flow by-passing of the most highly contaminated region. This could lead to significant deviations from equilibrium conditions. Evaluation of this point will require additional future research.

Residual Saturation Morphology

As was noted in the previous section, heterogeneity is expected in terms of the distribution of trapped NAPL in regions at residual saturation. This natural variation would be amplified by variability in the porous media characteristics. The morphology of the trapped NAPL (i.e., size of the trapped NAPL regions, volume to surface area ratio, and proximity to other trapped NAPL regions) will bear importantly on the rate at which the NAPL will be dissolved into a flowing groundwater phase.

Experiments were performed using a two-dimensional micro-model to relate physical and chemical factors of multiphase systems to the NAPL distributions noted at residual saturation. These studies showed that the viscosity and density of the NAPL were very important factors, while the velocity of the flowing groundwater had a minimal effect of the NAPL morphology—for typical ranges of groundwater velocities. This suggests that pump-and-treat methods will not be effective in mobilizing trapped NAPLs as a free phase. These results also suggest that as the density of a NAPL increases the surface area to volume ratio of the trapped NAPL will increase, thereby favoring local equilibrium conditions. More complete experimental and interpretation results of this work are given in a manuscript by Mayer and Miller, which will soon appear in **Transport in Porous Media**.

Important questions that remain to be answered are: the effect of dimensionality of the experimental system on the morphology of the trapped NAPL; and the derivation of the characteristics of a representative elementary volume, which is required to perform meaningful experimental studies, as a function of physical and chemical system parameters.

Aqueous-Vapor Mass Transfer

Mass transfer from the aqueous phase to the vapor phase is important not just in multiphase systems but for contaminant fate and transport for any volatile organic solute. This issue has become increasingly important in recent years as vacuum extraction has become a common method of subsurface restoration.

A series of experiments were performed in this work to determine the rate at which mass transfer occurs from the aqueous phase to the vapor as a function of key system variables. The results of this work were interpreted using two modeling approaches: a simple analytical model that ignored longitudinal dispersion, and a two-dimensional finite element model that included the effect of longitudinal dispersion.

The key results of this phase of the work were:

1. The liquid-phase mass transfer coefficient of toluene in water (used as a model compound) increased about one order of magnitude for every two order of magnitude increase in the liquid-phase velocity.
2. Liquid-phase resistance was found to dominate the overall mass transfer resistance for toluene.
3. Field-scale simulations showed that under ambient conditions, significant portions of a subsurface system would not be described accurately using an equilibrium assumption.
4. Field-scale simulations of a vapor-extraction scenario showed that a typical aquifer system was far removed from equilibrium solute distribution conditions.

Publications and Technical Reports

Journals and Proceedings

1. Mayer, A.S. and C.T. Miller (1990) A compositional model for simulating multiphase flow, transport and mass transfer in groundwater systems, Proceedings of the Eighth International Conference on Computational Methods in Water Resources, Venice, Italy, Computational Methods in Subsurface Hydrology, Edited by: G. Gambolati, A. Rinaldo, C.A. Brebbia, W.G. Gray, and G.F. Pinder, Computational Mechanics Publications, Southampton, U.K. and Springer-Verlag, Berlin, pp. 217-222.
2. Mayer, A.S. and C.T. Miller (1990) Equilibrium and mass transfer limited approaches to modeling multiphase groundwater systems, Proceedings of the 1990 National Conference on Environmental Engineering, American Society of Civil Engineers, Washington, DC, 9-11 July 1990.
3. Miller, C.T., M.M. Poirier-McNeill, and A.S. Mayer (1990) Dissolution of trapped nonaqueous phase liquids: mass transfer characteristics, Water Resources Research, Vol. 26, No. 11, pp. 2783-2796.
4. Mayer, A.S. and C.T. Miller (1991) Pore-scale distributions of nonaqueous phase liquids at residual saturation, In Press: Transport in Porous Media.

Published Abstracts and National Meeting Presentations

1. Mayer, A.S., C.T. Miller, and M.M. McNeill (1988) Mass transfer from non-aqueous phase liquids to the aqueous phase in groundwater systems, EOS Transactions, American Geophysical Union, Vol. 69, No. 44, p. 1189. Presented at American Geophysical Union Fall Meeting, San Francisco, California, 5-9 December 1988.
2. Mayer, A.S., and C.T. Miller (1989) Simulation of NAPL distributions in groundwater systems, using a laboratory pore-scale model, EOS Transactions, American Geophysical Union, Vol. 70, No. 15, p. 337. Presented at American Geophysical Union Spring Meeting, Baltimore, Maryland, 7-12 May 1989.
3. McNeill, M.M., C.T. Miller, and A.S. Mayer (1989) NAPL-aqueous phase mass transfer in groundwater systems, EOS Transactions, American Geophysical Union, Vol. 70, No. 15, p. 340. Presented at American Geophysical Union Spring Meeting, Baltimore, Maryland, 7-12 May 1989.
4. Szatkowski, A., and C.T. Miller (1989) An investigation of mass transfer at the unsaturated-saturated zone interface, EOS Transactions, American Geophysical Union, Vol. 70, No. 15, p. 325. Presented at American Geophysical Union Spring Meeting, Baltimore, Maryland, 7-12 May 1989.
5. Mayer, A.S., C.T. Miller, and F.A. Richard (1989) A finite element, multiphase flow and transport model incorporating nonequilibrium mass transfer relationships, EOS Transactions, American Geophysical Union, Vol. 70, No. 43, p. 1087. Presented at American Geophysical Union Fall Meeting, San Francisco, California, 4-8 December 1989.
6. Szatkowski, A., and C.T. Miller (1989) Vapor-aqueous phase mass transfer at the unsaturated-saturated zone interface, EOS Transactions, American Geophysical Union,

- Vol. 70, No. 43, p. 1093. Presented at American Geophysical Union Fall Meeting, San Francisco, California, 4–8 December 1989.
7. Miller, C.T., A. Szatkowski, A., M.M. Poirier-McNeill, and J.A. Pedit (1990) Interphase mass transfer in multiphase systems, EOS Transactions, American Geophysical Union, Vol. 71, No. 17, p. 497. Presented at American Geophysical Union Spring Meeting, Baltimore, Maryland, 29 May–1 June 1990.
 8. Mayer, A.S., and C.T. Miller (1990) Modeling interphase mass transfer processes in multiphase systems, EOS Transactions, American Geophysical Union, Vol. 71, No. 17, pp. 497–498. Presented at American Geophysical Union Spring Meeting, Baltimore, Maryland, 29 May–1 June 1990.
 9. Mayer, A.S., and C.T. Miller (1990) Pore-scale observations of nonaqueous phase liquids in a state of residual saturation, EOS Transactions, American Geophysical Union, Vol. 71, No. 43, p. 1310–1311. Presented at American Geophysical Union Fall Meeting, San Francisco, California, 3–7 December 1990.
 10. Mayer, A.S., and C.T. Miller (1991) Two-Dimensional Simulations of Residual Non-aqueous Phase Liquid Dissolution in Heterogeneous Porous Media, Submitted: EOS Transactions, American Geophysical Union. To be presented at American Geophysical Union Spring Meeting, Baltimore, Maryland, 28 May–1 June 1991.

PhD Dissertations and MS Technical Reports

1. Poirier-McNeill, Michele M. (1989) Mass Transfer from Non-Aqueous Phase Liquids to the Aqueous Phase in Groundwater Systems, MS Technical Report, The University of North Carolina, Chapel Hill, North Carolina.
2. Szatkowski, Andrew (1990) An Investigation of Interphase Mass Transfer at the Saturated-Unsaturated Zone Interface, MS Technical Report, The University of North Carolina, Chapel Hill, North Carolina.
3. Mayer, Alex S. (1991) An Analysis of the Physico-Chemical Factors Influencing Non-aqueous Phase Liquid Dissolution in Multiphase Groundwater Systems, In progress: PhD Dissertation, The University of North Carolina, Chapel Hill, North Carolina.
4. Vancho, Laura A. (—) An Experimental Investigation of Interphase Mass Transfer Phenomena in Multiphase Porous Media Systems, In progress: MS Technical Report, The University of North Carolina, Chapel Hill, North Carolina.

Participating Scientific Personnel

1. Cass T. Miller—was the principal investigator for the project. He was supported at the rate of 25% effort from the project, which was consistent with his effort expended. He directed all experimental and modeling work, and he participated actively in the presentation and publication of results derived from the project. He was the advisor for all MS and PhD documents derived from this project (previously listed), and he continues to work to produce additional publications from data generated during this research project.
2. Michele M. Poirier-McNeill—was supported for slightly more than two years as a research assistant. She performed most of the NAPL-aqueous phase mass transfer experimental work, based her MS technical report on this work (cited in project publications), co-authored a refereed publication and three published abstracts and national meeting presentations.
3. Andrew Szatkowski—was supported for slightly more than two years as a research assistant. He performed most of the aqueous-vapor phase mass transfer experimental work. His MS technical report was based upon this work (cited in project publications). He co-authored three published abstracts and national meeting presentations, and the final publication of his MS work is expected to result in three additional refereed publications.
4. Alex S. Mayer—was supported throughout the project as a research assistant. He assisted in conducting the NAPL-aqueous phase mass transfer experimental work, performed all of the micro-model experiments, assisted in the NAPL-vapor phase mass transfer work, wrote the one-dimensional multiphase flow and transport model, and is currently completing a two-dimensional multiphase flow and transport model. Mr. Mayer's PhD dissertation (cited in project publications) is based upon work on this project; it will be complete within the next few months. Mr. Mayer's work on this project has already resulted in co-authorship of four manuscripts and six published abstracts and national meeting presentations. The completion of his work will yield several additional publishable works.
5. Fred A. Richard—was supported for about one year as a research assistant. He developed an analytical solution used in reduction of the NAPL-aqueous phase mass transfer work and he assisted in the development of the one-dimensional multiphase flow and transport model.
6. Michael M. Hughes—was supported for about three months on the project as a research assistant. He assisted in the computer science aspects of the project.
7. Laura A. Vancho—was supported for four months as a research assistant. She assisted in the performance of NAPL-vapor mass transfer experiments. She will continue to pursue her MS research in this area.

Reports or Inventions

Patents will not be sought on any experimental or mathematical model developments accomplished in this work. All details of experimental procedures and computer codes have been or will be published and are considered to be in the public domain.

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